

METHOD OF PRODUCING A LIGHT-EMITTING DIODE

5 Cross-Reference to Related Application:

This is a divisional of application No. 10/324,848, filed December 20, 2002, which was a divisional of application No. 09/283,907, filed April 1, 1999, now U.S. Patent No. 6,559,075, which was a continuation of International
10 Application PCT/DE97/02261, filed October 1, 1997, which designated the United States, and which was not published in English.

Background of the Invention:

15 Field of the Invention:

The invention lies in the field of semiconductor manufacture. Specifically, the invention relates to a method of producing a light-emitting diode.

20 The term material layers is intended here to mean both layers of a single material and layer sequences or layer structures of different materials.

The production of products from semiconductors, for example
25 electronic and optoelectronic components, typically requires a plurality of process steps, including the processes needed for

growing semiconductor crystals and semiconductor layers, and for selective local removal and structuring of the layers. Many components consist in part of layer sequences of non-identical semiconductor materials, which are epitaxially
5 grown in monocrystalline form on a substrate.

As the process steps for structuring semiconductor layers or for separating two semiconductor layers from one another, etching processes are customarily used which erode the
10 semiconductor layers starting from the semiconductor surface. Such processes often take place very slowly and require corrosive chemicals. Further, not every known semiconductor material system has an etching process which allows corresponding layers to be structured with tolerable outlay.

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In particular, the semiconductor materials indium nitride, gallium nitride and aluminum nitride (InN, GaN and AlN) and mixed crystals or alloys thereof, which will be referred to together in the text below as "group III nitrides", are very
20 difficult to etch chemically. No reliable wet chemical etching process is currently available for this material system. It is therefore necessary to use the technically very elaborate process of reactive ion etching (dry etching). However, this process allows only relatively low etching rates
25 and requires poisonous and toxic gases (for example boron trichloride). Because etching processes act on the surface,

it is usually necessary to control the rate and duration of the etching accurately in order to reach the desired depth.

Further, for some semiconductor materials, for example and in particular for group III nitrides, bulk crystals of them or of lattice-matched semiconductor materials cannot be produced, or can be produced only with great technical outlay. Substrates for growing such semiconductor layers are therefore only of very limited availability. For this reason it is common practice, in order to grow these semiconductor layers, as a replacement to use substrates of other materials which have properties unsatisfactory for subsequent process steps or for the operation of the component. For the growth of group III nitride layers, these are, for example, sapphire or silicon carbide substrates.

These "replacement" substrates entail problems such as unsuitable atomic lattice spacings and different coefficients of thermal expansion, which have detrimental effects on the material quality of the semiconductor layers grown on them. Further, some process steps such as the known cleavage of semiconductor layers in order to produce resonator mirrors of laser diodes in GaAs, are difficult or even impossible with these substrates.

In order to overcome these problems, various processes alternative to etching have to date been proposed for separating semiconductor layers or other layers from one another or from a problematic substrate.

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In E. Yablonovitch et al., Appl. Phys. Lett. 51, 2222 (1987), U.S. Patent 4,846,931, Thomas J. Gmitter and E. Yablonovitch, July 11, 1989, it has been proposed to implement AlAs sacrificial layers in the GaAs/AlAs material system during the production process, which can then be dissolved using wet chemical means. This makes it possible to separate layers or structures from the substrate. However, because of the low lateral etching rate, this process is very time-consuming. For group III nitrides, furthermore, there exists no wet chemical etchant.

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U.S. Patent No. 4,448,636 describes a process for removing metal films from a substrate. There, the metal film is heated by light. An organic sacrificial layer between the substrate and the metal film is vaporized by the heat delivered and allows the metal layer to be removed. These organic intermediate layers cannot be employed, in particular, in the epitaxial growth of group III nitrides.

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A comparable process has been described for removing silicon dioxide layers from gallium arsenide in Y.-F. Lu, Y. Aoyagi,

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Jpn. J. Appl. Phys. 34, L1669 (1995). There, as well, an organic intermediate layer is heated by light absorption and the SiO₂ layer is lifted off.

- 5 Y.-F. Lu et al., Jpn. J. Appl. Phys. 33, L324 (1994) further discloses the separation of SiO₂ strips from a GaAs layer using an excimer laser.

German patent DE 35 08 469 C2 describes a process for
10 structuring layer sequences applied to a transparent substrate, in which the layers to be structured are exposed to laser radiation locally through a transparent substrate, and this laser radiation is absorbed in the layer to be structured.

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Further, so-called laser ablation has been applied to many material systems in order to remove material. In this process, however, the surface is always destructively eroded and separation in two parts that can be used further is not
20 possible.

Specifically for group III nitrides, Leonard and Bedair, Appl. Phys. Lett. 68, 794 (1996) describe the etching of GaN with a laser pulse under HCl gas and attribute it to a photochemical
25 reaction involving hydrochloric acid.

Morimoto, J. Electrochem. Soc. 121, 1383 (1974) and Groh et al., physica status solidi (a) 26, 353 (1974) describe the thermally activated decomposition of GaN.

5 In Kelly et al., Appl. Phys. Lett. 69 (12), Sept. 16, 1996, p.1749-51 it is shown that group III nitrides can be laser-induced to undergo thermally activated composition. However, that process likewise involves a process that acts on the surface of the semiconductor layer and, in particular, leads
10 to the destruction of the surface.

Summary of the Invention:

It is accordingly an object of the invention to provide an improved method of separating two layers of material from one
15 another, which overcomes the above-mentioned disadvantages of the heretofore-known devices and processes of this general type and which is not subject to destruction, or only slight destruction, of the free surfaces of the semiconductor layers. The object is, in particular, to develop a process for
20 separating group III nitride layers from sapphire or SiC substrates.

With the foregoing and other objects in view there is provided, in accordance with the invention, a process for
25 separating two layers of material from one another and

substantially completely preserving each of the two layers of material. The process comprises the following steps:

providing two layers of material having an interface boundary between the two layers;

5 irradiating the interface boundary between the two layers or a region in vicinity of the interface boundary with electromagnetic radiation through one of the two layers;

absorbing the electromagnetic radiation at the interface or in the region in the vicinity of the interface and inducing a
10 material at the interface boundary to decompose; and

separating the two layers of material.

In accordance with an added feature of the invention, a sacrificial layer is formed at the interface boundary and
15 wherein the absorbing step comprises absorbing the radiation with the sacrificial layer and decomposing the sacrificial layer.

In accordance with an additional feature of the invention, the
20 sacrificial layer is formed of a material having an optical band gap smaller than a band gap of one of the two layers.

In accordance with another feature of the invention, the decomposition is induced by converting an energy of the absorbed radiation into heat.

5 In accordance with a further feature of the invention, a temperature-sensitive sacrificial layer is formed at the boundary interface, and the absorbing step comprises absorbing the radiation in a part of one of the layers of material, diffusing the energy in form of heat into the temperature-
10 sensitive sacrificial layer, and decomposing the sacrificial layer.

In accordance with again an added feature of the invention, the decomposition of the interface boundary is induced by
15 generating gas, by means of a chemical reaction, sublimation, or another process, at the interface boundary with energy of the absorbed radiation.

In accordance with again an additional feature of the
20 invention, one of the two layers of material is a substrate and the other of the two layers of material is a semiconductor layer, a semiconductor layer sequence, or a semiconductor layer structure, and the irradiating step comprises radiating the electromagnetic radiation through the substrate.
25 Preferably, the semiconductor body is applied for mechanical stabilization on a support material.

In accordance with again another feature of the invention, the irradiating step comprises exposing the material to one or more light pulses. In a preferred mode, two or more coherent laser beams produce an interference pattern in the exposure.

5 The local radiation intensity is thereby increased.

In accordance with again a further feature of the invention, the semiconductor body consists at least partially of GaN, AlN, InN, mixed crystals thereof, layer sequences, layer
10 structures, and component structures thereof. Where the sacrificial layer is provided, it consists at least partially of a GaN, AlN, InN, or mixed crystals thereof.

With the above and other objects in view there is also
15 provided, in accordance with the invention, a process for laterally structuring a semiconductor layer or a semiconductor layer sequence disposed on a substrate. The novel process comprises the following steps:

providing a substrate and a body of semiconductor material
20 consisting essentially of at least one group III nitride material on the substrate, with an interface formed between the substrate and the semiconductor material;

The invention thus proposes to separate the two materials in
25 that, through one of the two layers of material, the

interface, or a region in the vicinity of the interface between the two layers, is exposed to electromagnetic radiation, and that a layer of material at or in proximity to the interface is decomposed by absorption of the radiation.

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This process is an alternative to wet and dry chemical etching processes as are used in semiconductor technology for structuring and producing individual layers and components.

It differs from them essentially in that it acts directly on
10 an internal region at the interface between the two layers and not on the free surface. This makes it possible, amongst other things, to produce the desired structuring depth directly instead of, for example, defining it by accurately setting the duration and rate of the etching. In the method
15 according to the invention, in addition, there is no destruction of one of the two layers of material. This leads to a novel possibility for detaching layer systems from one another or from the substrate. Cantilevered components or layers have advantages in further process steps; they are
20 suitable, for example, as substrates for homoepitaxy without the problems of lattice mismatching and the differences in the coefficients of thermal expansion, or to produce optical components (laser diodes) through the possibility of cleavage irrespective of the substrate cleavability. The transfer of
25 layers, layer systems and components of group III nitride materials to other substrates permits compatibility and

integration of group III nitrides with other technologically relevant semiconductor systems such as silicon.

The process makes it possible to separate layers of a
5 layer/substrate system through direct highly local action on internal interfaces or regions in proximity to interfaces. In general, the process described here can be applied to material systems in which the interface to be separated can be reached with electromagnetic radiation, in particular with light, the
10 radiation is absorbed by a material at this interface, and in which material in proximity to the interface can be decomposed by the absorption of light or light pulses. The process is facilitated if at least one decomposition product is in the form of gas. Examples of suitable semiconductor materials for
15 this process include group III nitrides, oxide materials and Si_3N_4 .

Optoelectronic components such as light-emitting diodes and semiconductor lasers and electronic components such as
20 transistors, diodes, surface acoustic wave components are typically produced in large numbers on a single substrate. In this case, the described process of light-induced structuring can be used for separating the individual components. The separation of the components from the substrate may, as
25 mentioned above, take place through the decomposition of a sacrificial layer which needs to be introduced during the

fabrication process under or over the surface to be separated. Thin InGaN layers are especially suitable for this because of their comparatively small band gap and their chemical stability.

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The production of freestanding layers and layer sequences makes it possible to transfer layers of group III nitrides to other substrates (for example silicon) which may differ greatly in terms of their structural, mechanical and thermal properties from those of group III nitrides. The procedure makes it possible to combine light-emitting diodes and semiconductor lasers made of group III nitrides with conventional support materials for the production of flat display screens or the integration of such components in circuits and integrated circuitry. Cantilevered layer structures can also be used as optical waveguides and optical couplers. If this is structured with a diffraction grating, the light can be coupled in through the grating. Layers of specific thickness can also be employed as optical filters.

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By means of exposure through a mask, exposure with coherent light beams combined with interference patterning, holography, or serial or simultaneous exposure of various selected locations, lateral structuring of one of the layers of material can be produced.

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The essential steps in the method according to the invention are as follows:

- (i) identification, selection or production of an interface to be separated in the desired layer system, which can be reached by the radiation to be used for separation;
- (ii) identification of a material, or incorporation of a material as a sacrificial layer at the interface, which material absorbs the incident light; or
- (iii) identification or incorporation of a material as a sacrificial layer in proximity to the interface, which material can be made to decompose by the absorbed light or by the energy resulting therefrom, and produces a product in gas form in sufficient quantity during the decomposition; and
- (iv) exposure to radiation of a selected wavelength and intensity, so that the radiation is predominantly absorbed by the interface to be separated or by the sacrificial layer, and thereby stimulates the decomposition reaction, in the case of transparent substrates it also being possible for the interface or sacrificial layer to be exposed through the substrate.

The method according to the invention is, in particular, also usable for structuring semiconductor layers consisting of

group III nitrides which, for example, are applied to SiC or sapphire substrates.

Other features which are considered as characteristic for the invention are set forth in the appended claims.

Although the invention is illustrated and described herein as embodied in a method of producing a light-emitting diode, it is nevertheless not intended to be limited to the details shown, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and process of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific embodiments when read in connection with the accompanying drawings.

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Brief Description of the Drawings:

Fig. 1 is a partial schematic sectional side view of a first exemplary embodiment of the invention;

Fig. 2 is a partial schematic sectional side view of a second exemplary embodiment of the invention;

Fig. 3 is a partial schematic sectional side view of a third exemplary embodiment of the invention;

Fig. 4 is a partial schematic sectional side view of a fourth
5 exemplary embodiment of the invention;

Fig. 5 is a partial schematic sectional side view of a fifth exemplary embodiment of the invention;

10 Fig. 6 is a partial schematic sectional side view of a sixth exemplary embodiment of the invention;

Fig. 7 is a partial schematic sectional side view of a seventh exemplary embodiment of the invention;

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Fig. 8 is a partial schematic sectional side view of a eighth exemplary embodiment of the invention; and

Fig. 9 is a partial schematic sectional side view of a ninth
20 exemplary embodiment of the invention.

Equivalent or functional equivalent components and features in the figures are identified with the same reference symbol throughout.

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Description of the Preferred Embodiments:

Referring now to the figures of the drawing in detail and first, particularly, to Fig. 1 thereof, there is seen a first embodiment with an interface of a layer system made up of a first semiconductor layer 2 and of a second semiconductor layer 4. The layer system is exposed to a laser beam 1 through the first semiconductor layer 2. The light is strongly absorbed in the material of the second semiconductor layer 4. The first semiconductor layer 2 is transparent to the laser beam 1.

The energy absorbed in the second semiconductor layer 4, predominantly in proximity to the interface between the two semiconductor layers 2, 4, induces for example decomposition of the semiconductor material of the second semiconductor layer 4 in that region. This brings about the separation of the two semiconductor layers 2 and 4. Examples of possible decomposition mechanisms include sublimation or chemical reactions. The decomposition may in this case be both thermally and photochemically initiated. The separation is, in particular, reinforced if products in gas form are produced during the decomposition.

It is, however, also possible for the energy absorbed in the semiconductor layer 4 to diffuse into the semiconductor material 2 and for the decomposition to take place there. The

relative thickness of the two semiconductor materials may in this case vary greatly. The equal thickness measurements of Fig. 1 are not necessary. In that regard, the figures of the drawings are not necessarily drawn to scale.

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One much-used process of producing semiconductor materials is growth on substrates. In terms of the process presented here, the distinction between substrate and semiconductor material is irrelevant. One possibility is for the semiconductor
10 layers 2, 4 to be grown on a substrate and for the separation to take place at the interface between the semiconductor layers 2, 4.

In the illustrative embodiment in Fig. 2, a semiconductor
15 layer 4 is separated from a substrate 6. In order to do this, the semiconductor layer 4 is exposed to light 1 through the substrate 6 and the radiation energy is absorbed in the material of the semiconductor layer 4. Depending on the absorption properties, it may however also be possible to
20 expose the interface through the semiconductor layer 4 so that the substrate 6 absorbs the light energy. As already presented above, it is not however necessary for the decomposition to take place in the absorbing part of the structure, and the energy may where appropriate also diffuse
25 into the other part and bring about the decomposition there.

The semiconductor layers 2, 4 may either each be homogeneous layers of one semiconductor, or consist of layer sequences of different semiconductors, as indicated with reference to the example of the semiconductor layer 4 in Fig. 3. These layer
5 sequences may already contain an actual component preprocessed or fully processed, even in the form of an integrated electronic or optoelectronic circuit. All these structures are in the context of the application to be interpreted as semiconductor layers.

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In order to improve and deliberately affect the absorption of the light at the interface to be separated, in accordance with the fourth illustrative embodiment according to Fig. 4 a special absorbing layer 8 may be interposed between a first
15 semiconductor layer 2 and a second semiconductor layer 4, or between the substrate 6 and the semiconductor layer 4 (cf. Fig. 2). The absorbing layer 8, for example a semiconductor layer, has for example an optical band gap which is smaller than that of the surrounding materials. The layer 8 can then
20 itself be decomposed and therefore act as a sacrificial layer. It is, however, also possible for the absorbed energy to diffuse and lead to decomposition and separation in proximity to the layer 8.

25 It is also possible for the energy to be absorbed in the semiconductor layer 4 but for the latter to be too stable to

become decomposed. In this case, the layer 8 may be selected in such a way that it decomposes particularly readily, and thus again functions as a sacrificial layer. One particular advantage of the process described here is that the layer 8
5 may be crystalline and lattice-matched.

The electromagnetic radiation must be selected in such a way that it can reach the interface to be separated and be absorbed sufficiently there. This can be done in the simplest
10 case by illumination using a lamp, if appropriate after filtering. If the photon flux which this provides is insufficient, the illumination may also be carried out using a suitable laser.

15 Particularly in the case of thermal decomposition, the heat may diffuse rapidly out of the region to be decomposed on account of the thermal conductivity of the materials. It may therefore be necessary to deliver the light energy in the form of very short light pulses, in order nevertheless to reach the
20 temperature needed for the decomposition.

The process described here may also be used for lateral structuring. This can be carried out using various procedures. A focused light beam can be employed for
25 sequentially exposing spatially separate points of the material and for bringing about the decomposition. As shown

in the illustrative embodiment in Fig. 5, it is possible to use an exposure mask 10 through which selected areas of the sample can be removed.

5 Likewise, in accordance with the illustrative embodiment in Fig. 6, exposure using holographic process is possible (for example exposure with an interference grating), in which the interference effects are utilized through simultaneous exposure to more than one coherent beam.

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The part separated by the interfacial decomposition may be very thin or small, and therefore mechanically unstable and difficult to process. It is possible to apply this part according to the illustrative embodiment in Fig. 7 before or
15 after the separation, for example using adhesive 12, to a new support material 14. This is represented by way of example for the case of fixing before the interfacial decomposition in Fig. 7.

20 After the separation, a thin semiconductor layer 4, separated from the substrate 6, is then available on the support material.

Particularly advantageously, the method according to the
25 invention may be used for the production of layer sequences 4 or complete component structures of electronic or

optoelectronic components, which are formed on nonconducting substrates. In these cases, it is often difficult, in addition to the electrical contact 16 arranged in each case on the other side of the layer sequence 4 or component structure from the substrate, to arrange an electrical contact on a semiconductor layer arranged in proximity to the substrate. In order to do this, complicated etching processes and the formation of mesa structures are usually necessary. With the process described here, according to the illustrative embodiment in Fig. 8 it is possible to detach layer sequences 4 or complete component structures from nonconducting substrates. The sides of the layer sequences 4 or component structures which are now free but previously faced the substrate are now readily accessible for electrical contacts 18.

The way in which this process is implemented depends on the material system. A preferred embodiment for semiconductor materials uses a material on the interface to be separated with a smaller band gap than all other layers or materials on one side of the interface. For exposure, a radiation wavelength is selected at which the radiation can penetrate as far as the interface, and which is absorbed by the material with smaller band gap. Decomposition in this or a neighboring material must thereby be inducible.

This process is particularly suitable for layers or layer systems of group III nitrides since this group of materials has some physical properties particularly advantageous for this process. Firstly, it is possible to heat group III
5 nitrides above their decomposition temperature in a spatially delimited and controlled way through the absorption of individual light pulses. At the temperatures produced by the absorption of light pulses, the decomposition of the nitrides and the formation of nitrogen gas is initiated (600°C -
10 1800°C , depending on the composition of the nitrides). Secondly, the described procedure is assisted by the fact that the melting points of group III nitrides are far higher than the decomposition temperatures, so that during the absorption of intense light pulses the layers and components do not
15 become damaged by melting. Thirdly, these semiconductor materials are especially suitable for optical processes since, as a function of the wavelength of the light, they have a well-defined sharp threshold, a direct band gap, at which they change from transparent to fully absorbing. Further, the
20 wavelength from which the absorption starts can be varied using mixed crystals of the nitrides (InGaN and AlGaN) over a wide spectral range (band gaps: InN 1.9 eV, GaN 3.4 eV, AlN 6.2 eV). In addition, group III nitrides are often produced on sapphire substrates which are transparent throughout the
25 optical and ultraviolet range. This even makes it possible to expose the layers through the substrate.

If the decomposition is thermally activated, it is important for it to be possible for the resultant heat to be concentrated onto the interface or the sacrificial layer, on the one hand in order to minimize the required incident intensity, and on the other hand in order to preclude the possibility of undesired effects on the surrounding material. Since the photogenerated quantity of heat is rapidly dissipated by the thermal conductivity of the materials out of the hot volumes, the requisite temperature must be produced in a very short time. This can be done using short laser pulses. For typical thermal conductivities of group III nitrides, the absorbed energy can be concentrated through the use of laser pulses with a period of 1 ns to 10 ns onto the penetration depth of the absorbed light or the thickness of the sacrificial layer. For the structuring and decomposition of group III nitrides, one suitable example is a "Q-switched" pulsed Nd:YAG laser.

As a specific embodiment for the photoinduced decomposition of the materials GaN and InGaN (band gaps between 1.9 and 3.4 eV), the third harmonic laser line of an Nd:YAG laser may be used. This laser line is produced, for example, using a nonlinear optical crystal and has a wavelength of 355 nm (3.5 eV). GaN and InGaN layers absorb these light pulses and can be made to decompose. AlGaIn layers and the customarily used sapphire substrate are transparent to this wavelength.

Cantilevered GaN and InGaN layers can be produced directly by decomposition of the substrate/layer interface. AlGaN layers and components can be detached from the substrate by photoinduced decomposition of thin GaN or InGaN sacrificial layers. Fig. 7 schematically shows the way of separating a GaN layer 4 from a sapphire substrate 6, polished on both sides. The interface between the GaN and the sapphire is exposed through the substrate to a single laser pulse of wavelength 355 nm. The laser radiation is absorbed by the GaN in proximity to the interface down to a depth of about 100 nm, as a result of which the interface becomes heated. If temperatures in excess of 850°C are reached, the GaN starts to decompose with the formation of nitrogen gas. For pulse energies of more than about 0.2 J/cm², the energy density is sufficient for complete decomposition at the boundary between the substrate 6 and the GaN layer 4, as a result of which the bond between the substrate 6 and GaN layer 4 is separated in the exposed area. In order to stabilize the cantilevered layer, the sample may be bonded using a resin or wax 12 to a support wafer or sheet 14 via the side of the layer prior to the exposure. If the GaN layer 4 is separated from the substrate 6 by the decomposition reaction, the sapphire substrate 6 can be lifted off and the GaN layer 4 remains behind on the support wafer or sheet 14. The wax or resin can then be dissolved in acetone and the GaN layer remains behind as a cantilevered layer.

When structuring GaN layers by exposing the interface through a sapphire substrate, GaN structures with nonvertical, that is to say oblique side faces can be produced, which, as Fig. 9 shows, propagate from the decomposition site. This process
5 can, for example, be used to produce structures 20 with a pointed or pyramidal design if the lateral width of the interference grating or the mask is matched to the layer thickness. This process also helps the production of cantilevered layers.

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Various components made of group III nitrides can be structured using the described procedures. The fabrication of periodic line gratings and surface structures by exposure with an interference grating can advantageously be used to produce
15 Bragg reflectors and distributed feedback lasers based on group III nitrides. It is also possible to obtain optical dispersion gratings, which if appropriate may also be used for transmitted light, through variation of the thickness of the layer by structuring with an interference grating. Pyramidal
20 structures of AlN and AlGaIn can, because of their negative electron affinity, be used as cold cathode emitters, for example, in flat display screens.